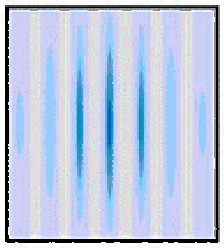

LOCAL STRUCTURE FROM DIFFRACTION

MICHIGAN STATE UNIVERSITY

The Nanostructure Problem

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Dept. Physics and Astronomy

Michigan State University.

NIRT STRUCTURE OF NANOCRYSTALS

Office of Basic Energy Sciences • Serving the Present, Shaping the Future

NSF

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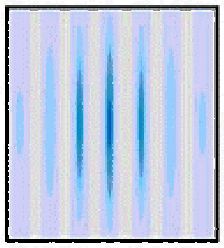
Summary



LOCAL STRUCTURE FROM DIFFRACTION

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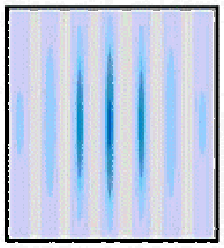
- Proposed DOE(/NSF) grand challenge

Solve the nanostructure problem

(robust, atomic resolution structure of nanoparticles)

The Nanostructure Problem



LOCAL STRUCTURE FROM DIFFRACTION

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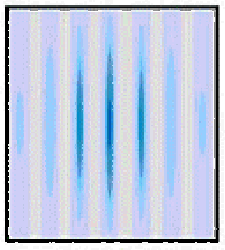
- Atomic Structure Underpins Materials Properties
  - Crystallography revolutionized Materials Science and Molecular Biology in the early/mid 20th Century
- Crystallography fails for nanostructured materials
  - Nanoparticles are not periodically long-range ordered, by definition
  - The nanostructure gives the particles their interesting properties – this is the *definition* of nanotechnology
- The Nanostructure problem
  - How do we get robust atomic resolution structural solutions from nanostructured materials?

The Nanostructure Problem



LOCAL STRUCTURE FROM DIFFRACTION

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The miracle of crystallography

1. Put a single crystal on your diffractometer
2. When everything goes well, software will tell you where the atoms are (Space group, lattice parameters, atomic coordinates)

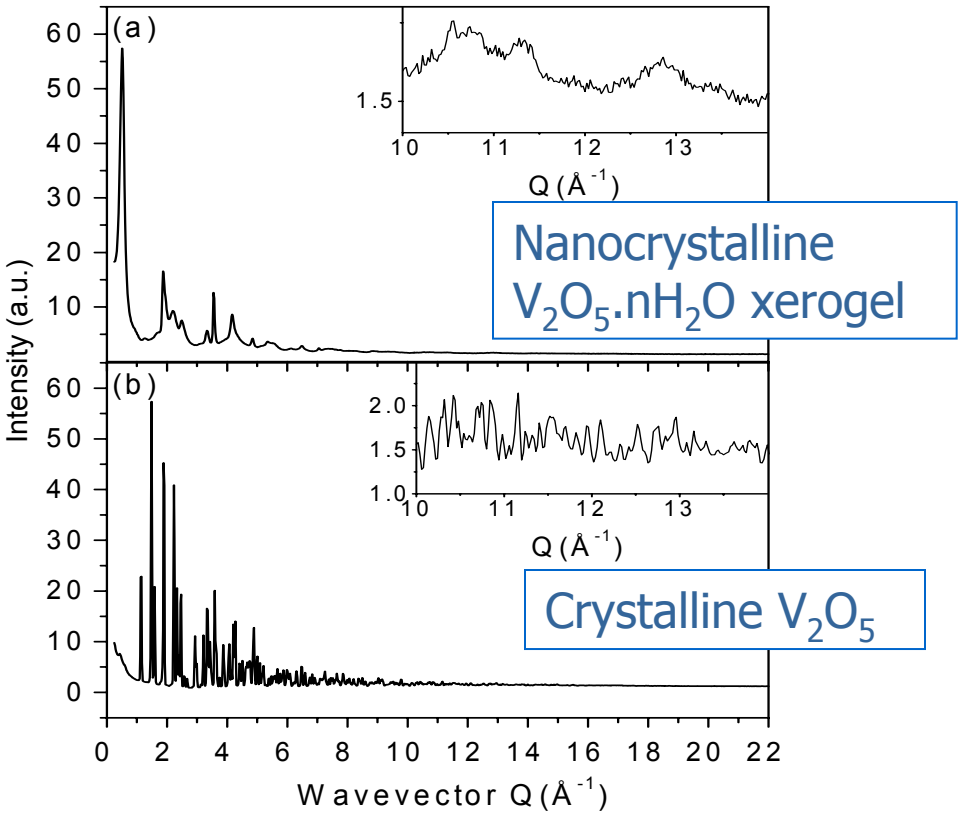
How does it work?

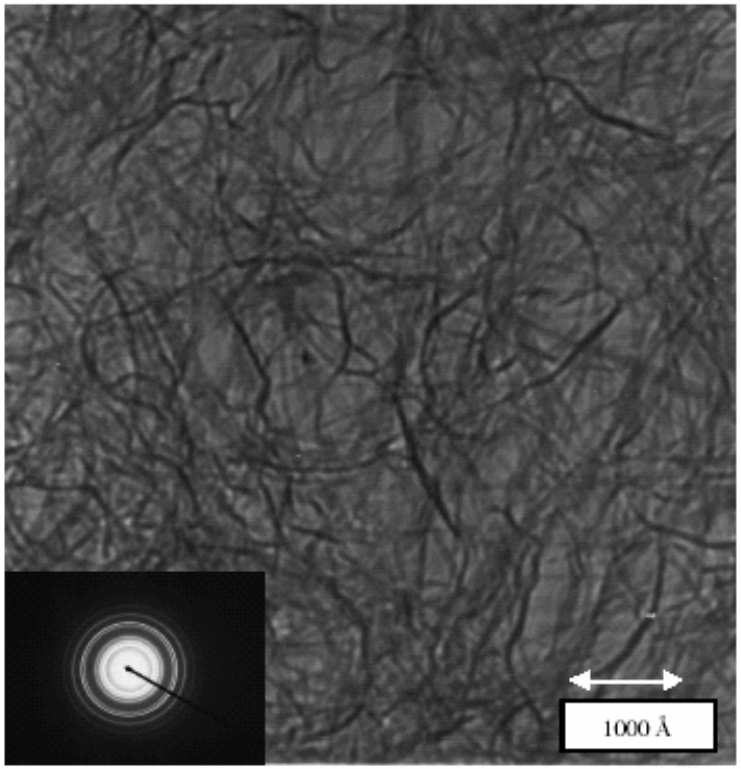
- The inverse problem is not directly invertable because of the loss of phase information, the “Phase Problem”

However,

- There is sufficient information in the data to reconstruct the structure with reasonable accuracy: there are many more Bragg peak intensities than information needed
- There are good algorithms for solving the non-linear optimization problem (direct methods, etc. etc.)

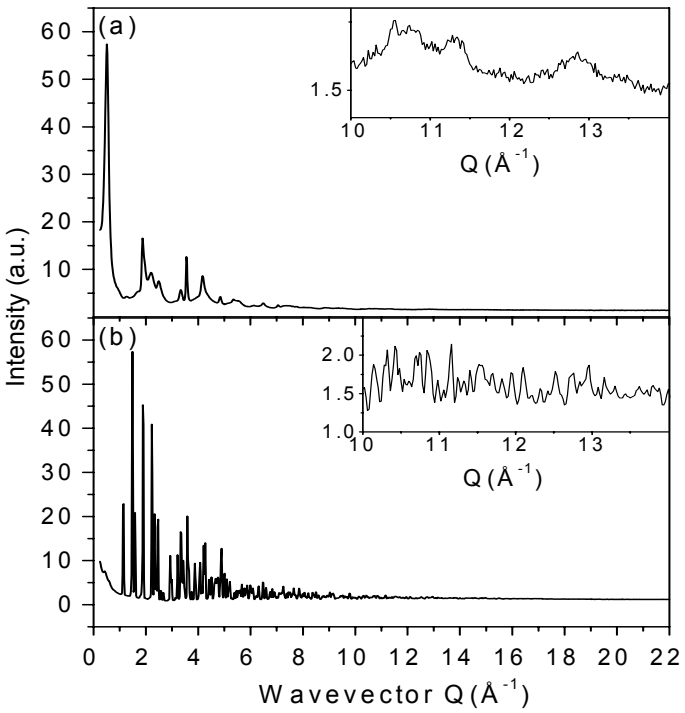
The Nanostructure Problem

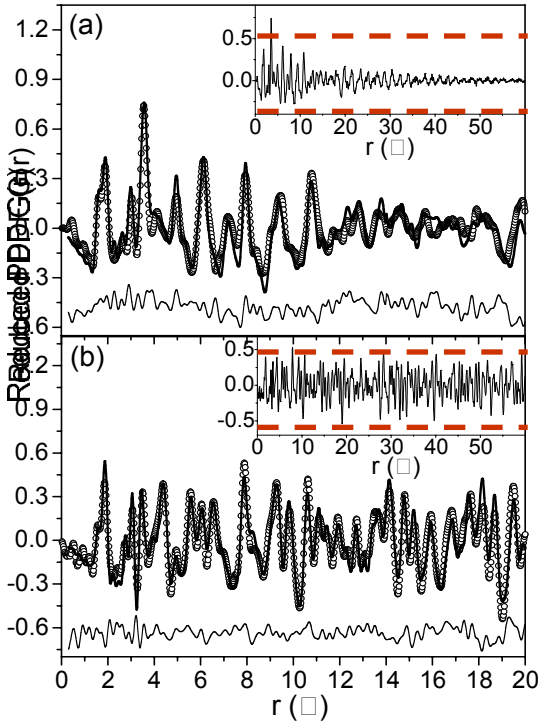




- Bragg peaks become broad and overlap => loss of information
- Structure becomes more complex => more information needed to specify it
- Crystallographic methods fail!

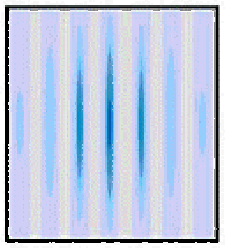
The Nanostructure problem





- Things are better in real-space using the atomic Pair Distribution Function (PDF) method (peaks are sharp in both cases).
- Structure models can be differentiated and refined
- However: No *ab-initio* structure solution method
  - Poor match between information required and information available
  - Algorithms not so well developed.

Solution to the Nanostructure Problem



LOCAL STRUCTURE FROM DIFFRACTION

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1. Make a well conditioned problem for nanostructures. Where necessary:
   1. Add constraints: Incorporate complementary data-sets (PDF, XAFS, NMR, imaging data…)
   2. Remove degrees of freedom: Incorporate prior knowledge (local symmetries, coordinations, etc.)
2. Have algorithms/programs to solve it

- Progress being made in Billinge-group (next few slides)
- Critical role for DOE facilities because of the need for complementary techniques

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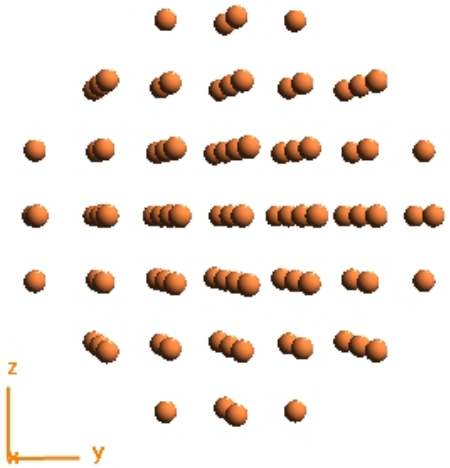
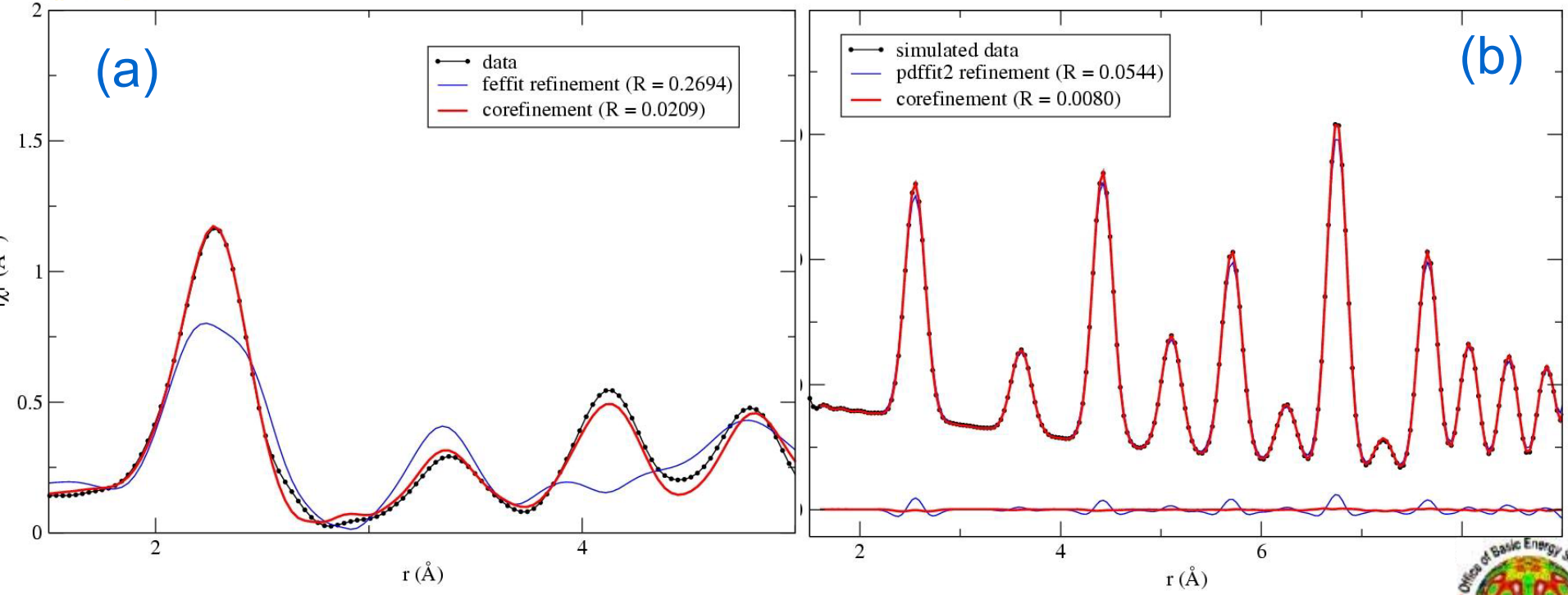
Billinge-group activities-1: Combining complementary datasets (XAFS and PDF)



1. Start with a distorted model for copper (blue curve in a)
2. Refine to PDF data (dots) alone (blue curve in b)
3. Refine to PDF and XAFS data together (red curve in a and b)



-refinement led to a better structural solution (preliminary result)

Rapid Acquisition PDF (RAPDF): Measuring PDFs in a few seconds

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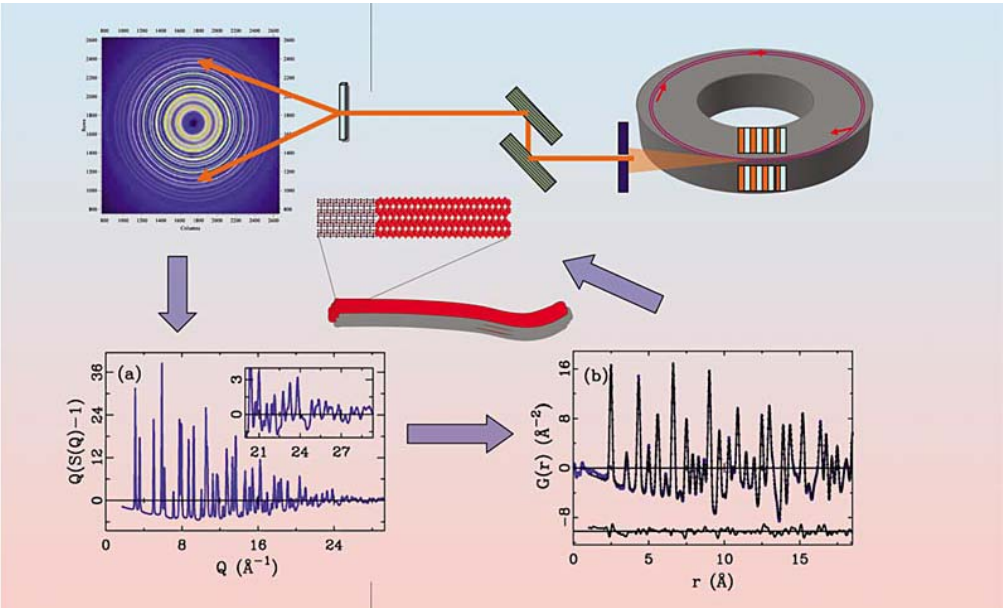

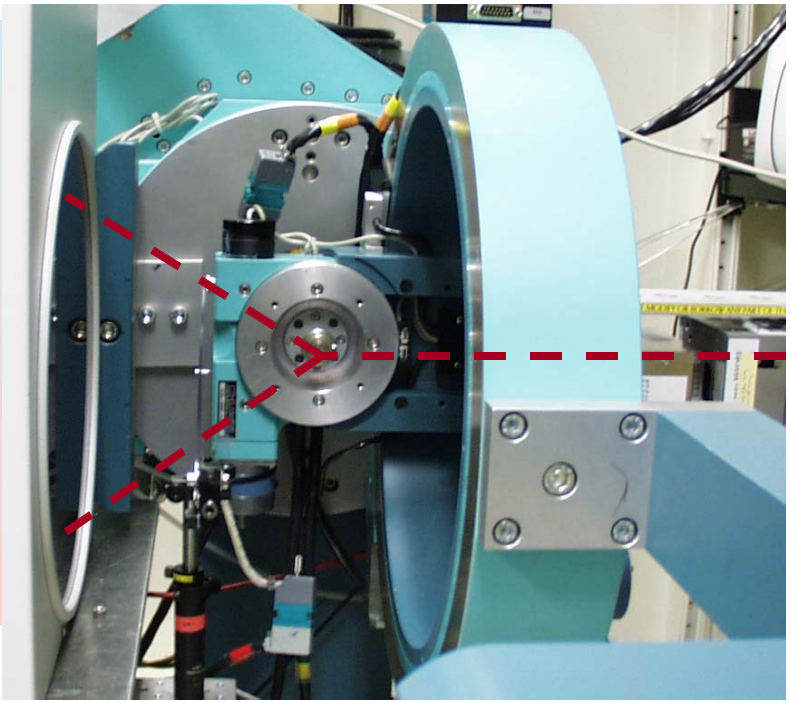

- Chupas et al., J. Appl. Crystallogr. (2003)

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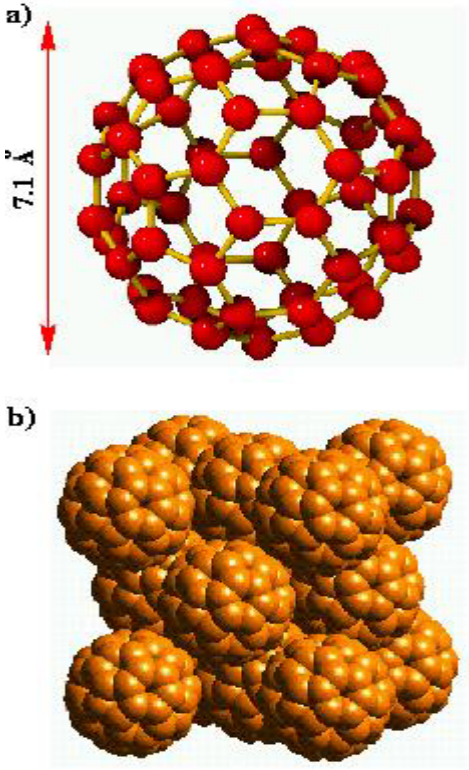
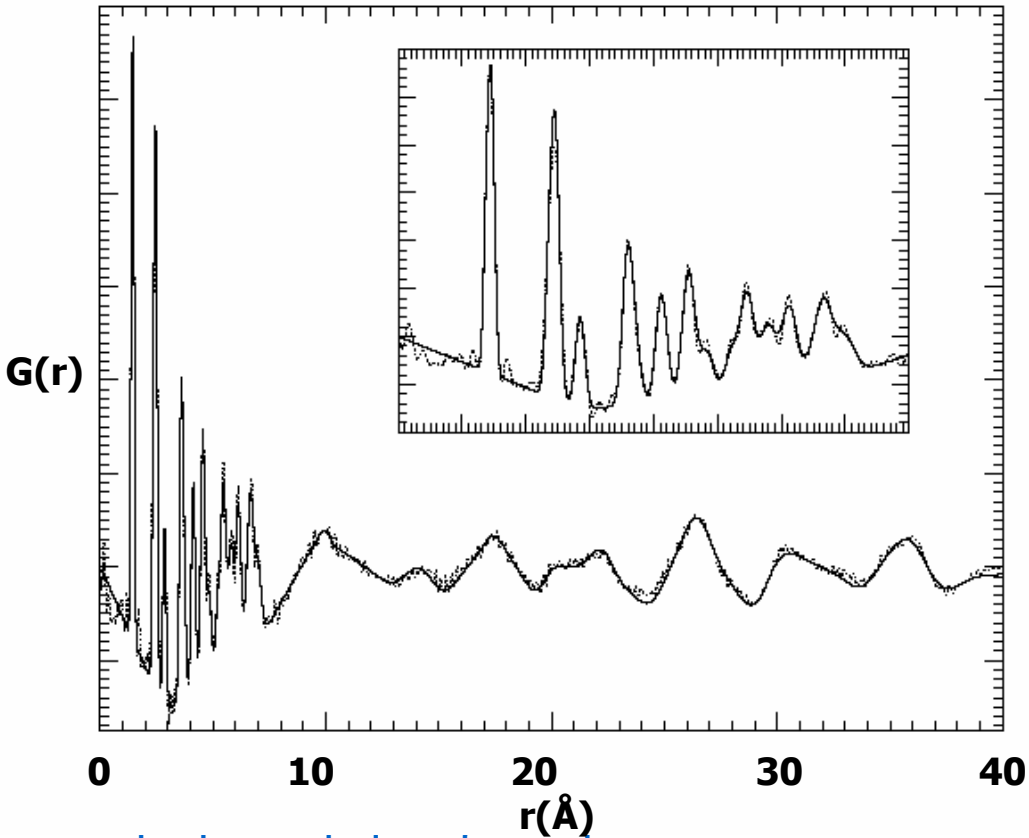
Modeling nanoscale clusters





- Nanoparticle structure modeling, intra- and interparticle information (collaboration with Ming Lei and Mike Thorpe)
- Excellent *quantitative* agreement for intra- and inter- particle order
- Now do something different: Start with random arrangement of atoms + PDF data and determine the structure *ab-initio*

Billinge-group activities-2: *ab-initio* structure solution directly from PDF data

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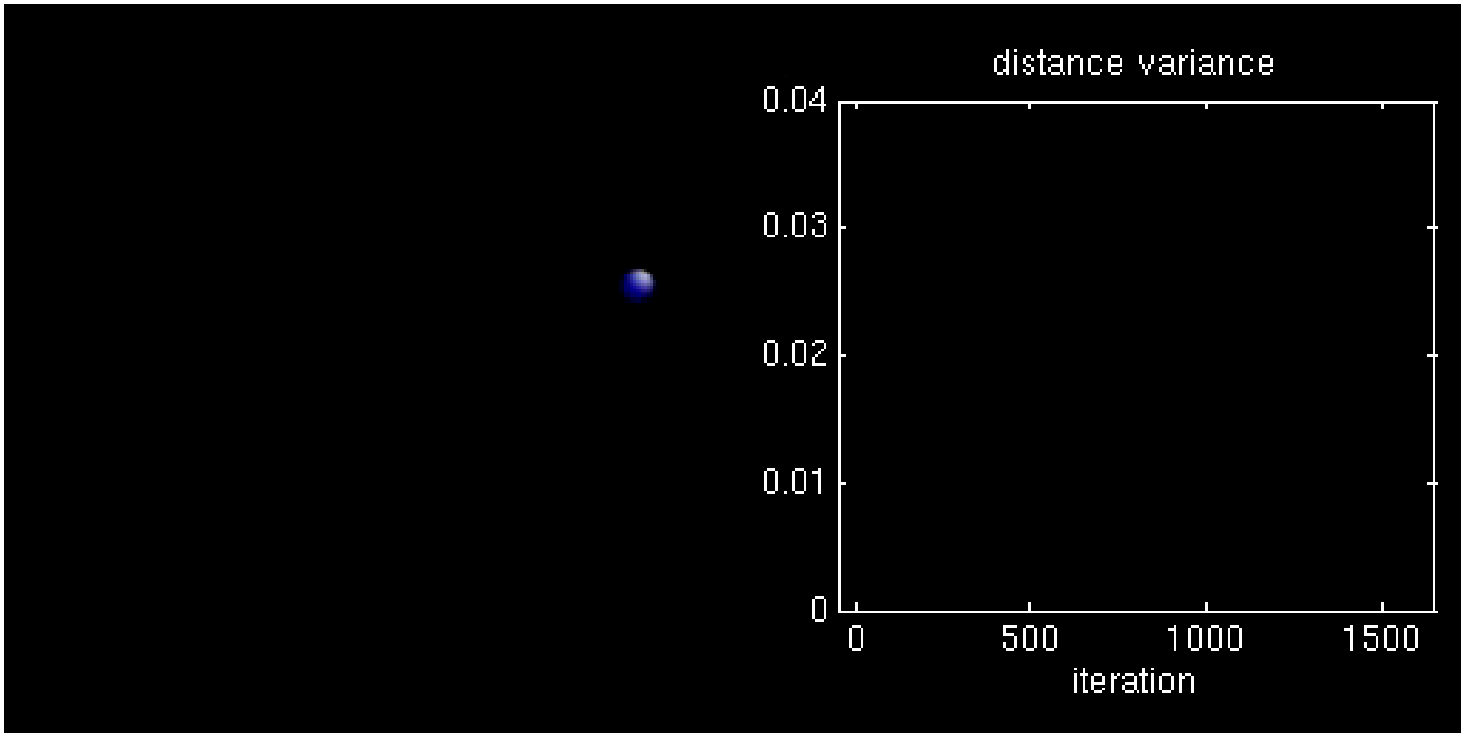

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Billinge-group activities-2: *ab-initio* structure solution directly from PDF data

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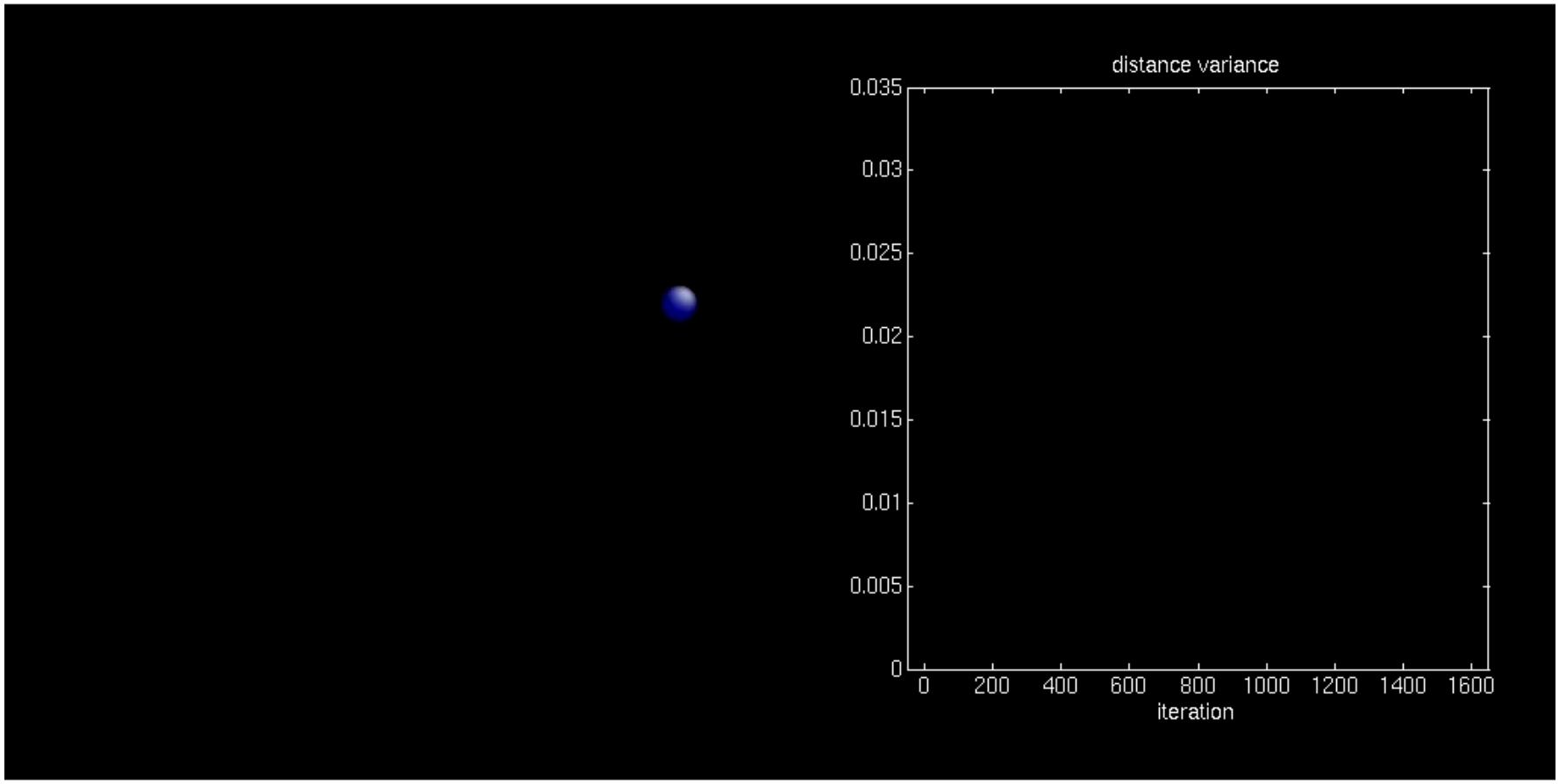

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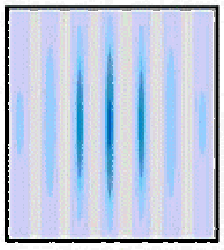
Summary



LOCAL STRUCTURE FROM DIFFRACTION

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- Proposed DOE(/NSF) Grand Challenge

  Solve the nanostructure problem

Possible routes forward:

- Role of DOE facilities =>coordinate and invest in beamlines for complementary techniques:
  - PDF/total scattering (x-ray, neutron, anomalous, isotopically substituted
  - XAFS
  - NMR
  - Imaging (TEM/STM/diffraction imaging…)
- Coordination of access and data analysis
  - Autonomous “Nanostructure Center”:
    - Clearing house for nanostructure determinations
    - Home for data analysis theory and computation developments

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